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POSITRON ANNIHILATION STUDIES OF VERY FINE STRUCTURED
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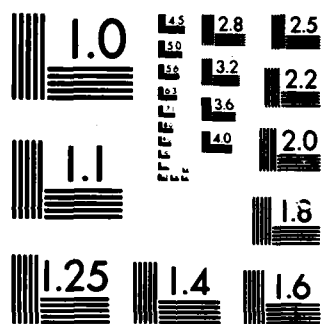
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Positron Annihilation Studies of Very Fine
Structured Materials

Final Report

Submitted by Phillip L. Jones

December 17, 1985

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ABSTRACT

An Fe-Nd-B permanent magnet alloy (Crumax 30) has been evaluated as a function of thermal treatment by means of positron annihilation lifetime spectroscopy. The results of this preliminary study indicate that the room temperature lifetime spectra can be accurately modeled using either a two-component or a partially constrained three-component fit. The thermally-induced variations in lifetime spectra can be correlated with the concomitant decrease in magnetic coercivity in a manner that is consistent with thermally-induced microstructural transformations reported in the literature. The demonstrated sensitivity of positron annihilation lifetime spectroscopy to thermally-induced changes in both microstructure and magnetic coercivity suggests that a more thorough systematic positron annihilation evaluation of Fe-R-B alloys could provide further insight into the relationship between processing, structure and magnetic properties.



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INTRODUCTION

Recent developments in materials processing have resulted in significantly improved properties in a wide variety of materials. The nanometer structural dimensions characteristic of these materials makes complete characterization difficult, however, further property enhancement will most likely necessitate a more thorough understanding of processing variables and resulting structure. Specifically, the purpose of this short-term research study was to determine the sensitivity of positron annihilation spectroscopy to thermally-induced changes in the magnetic coercivity of an Fe-Nd-B permanent magnet material. If this atomic-level nondestructive testing technique is sensitive to structural changes that influence observed coercivity, the additional structural information thus obtained combined with the results of more conventional testing techniques could lead to a more fundamental understanding of the relationship between processing, structure, and magnetic property enhancement.

EXPERIMENTAL PROCEDURES

Material

The material used in this study was a 3/8 inch diameter rod of sintered Fe-Nd-B supplied by Dr. Narasimhan, Magnetic Materials Division, Colt Industries. Due to the proprietary nature of this alloy, identified as Crumax 30, the specific chemical composition and thermal processing history is not available. A small amount of Dy was added to the material for the enhancement of linear demagnetization characteristics. The pertinent room temperature magnetic properties include: $(BH)_{max} = 33 \text{ MGOe}$, $B_r = 11.9 \text{ kG}$, and $\mu H_c = 11.1 \text{ kOe}$. Prior to sample fabrication, the rod was demagnetized by heating to 400C for 15 minutes. The rod was subsequently sectioned into three sample sets to facilitate positron annihilation spectroscopy, coercivity measurements and TEM studies on material with identical thermal histories.

Thermal Treatment

The coercivity of the starting material was varied by controlled elevated temperature exposure. The initial thermal treatment was performed at 400C in a vacuum of 2×10^{-6} torr. Two of the three sample sets were held at this temperature for 3 and 6 hours, respectively. This thermal treatment proved ineffective in decreasing coercivity. Subsequent attempts to reduce coercivity involved heating the sample set initially treated at 400C for six hours to 375C in vacuum and holding for an additional 9 hours. This treatment also proved to be ineffective. Lastly, the sample set initially treated for three hours at 400C was heated to 1150C for approximately 2.5 hours in ultra-high purity argon, which effectively reduced the coercivity to 0.1 kOe.

Positron Annihilation Spectroscopy

Positron lifetime experiments were performed using an EG&G Ortec standard fast-fast coincidence timing system. A complete description of the measurement system can be found in the literature [1]. The measurement

apparatus was enclosed within an environmentally stabilized chamber with temperature maintained at $22 \pm 0.5^\circ\text{C}$ to reduce the effects of temperature induced timing drift. Timing resolution was determined using the prompt curve arising from a Co^{60} source with the energy windows set for Na^{22} events. In this configuration the timing resolution was determined to be 260 psec. The Na^{22} positron source was placed between two thin (~ 0.2 mil) pieces of Ti foil, and had a strength of approximately 40 microcuries. Measurements were made using two identically treated 1/8 inch thick disks situated on opposite sides of the source in the normal sandwich configuration. The resulting sample-source-sample configuration resulted in spectra collection times of ~ 2.5 hours. Four spectra were collected for each sample condition and the results modeled using the PFPOSFIT computer program [2].

Coercivity Measurements

Complimentary coercivity measurements using identically treated samples were performed by Professor H. H. Stadelmaier and Dr. N. A. El-Masry at North Carolina State University. The coercivity (iH_c) was measured parallel to the '1/8 inch cubic samples' magnetically oriented direction using a maximum magnetic field of 30.0 kOe. The error associated with these measurements was ± 0.2 kOe.

RESULTS AND DISCUSSION

Positron lifetime spectra were collected for the Crumax 30 alloy as a function of thermal treatment and the results compared to measured changes in coercivity. The demagnetized as-received material exhibited a coercivity of 13.8 kOe. The sample treated at 400C for six hours and subsequently at 375C for 9 hours displayed a coercivity of 12.7 kOe, and will be referred to as the low temperature sample set in the remainder of this discussion. The sample treated at 400C for 3 hours and subsequently at 1150C for 2.5 hours exhibited a coercivity of 0.1 kOe, and will be referred to as the high temperature sample set in the remainder of this report. The following discussion of the positron annihilation lifetime behavior of this alloy as a function of thermal treatment is predicated on the spectra obtained from these three sample sets.

Two Component Fit

Attempts were made to fit the experimental spectra with either one, two, three, or four decaying exponentials with no constraints placed on any of the fitting parameters. The most consistent and statistically meaningful results were obtained for the two component fit. The lifetime and intensity components derived from this two component fit are correlated graphically with measured coercivity in Figure 1. The data points represent mean values, with the standard deviations obtained for the positron lifetime components given in Table I. The straight line segments connecting datum points are included to show trends, and are not intended to imply linear variations.

Both component lifetimes τ_1 and τ_2 were found to consistently increase with decreasing coercivity, with the largest increase associated with the low temperature sample. The two data points associated with the high temperature

sample (0.1 kOe) represent the resolved lifetime components obtained both before and after a gray surface scale was removed from the sample surfaces. The 1150C exposure had little effect on τ_1 while τ_2 exhibited a statistically significant increase. The corresponding component intensities I_1 and I_2 were not noted to change appreciably as the result of the low temperature heat treatment, but displayed statistically significant changes as the result of the 1150C exposure.

Although the resolved lifetime components obtained from the two component fit cannot be assigned to specific annihilation environments without further investigation, the observed variations noted as a function of thermal treatment warrant some discussion. Theoretically, each resolved lifetime component τ_i and corresponding intensity I_i can be attributed to a particular annihilation environment such as a bulk phase or a vacancy-type defect. Thermally or mechanically induced changes in specific components can then be attributed to changes in the local electron density (τ_i) and the relative concentration (I_i) of the specific annihilation environment. In addition, positron annihilation lifetime spectra contain a source-surface component which arises from both annihilation events occurring in the Na^{22} source encapsulation material and at the surface of the specimen in question.

The structure of sintered Fe-Nd-B alloys is quite complex, consisting of several equilibrium and metastable phases. Prior studies [3-5] indicate that sintered Fe-Nd-B consists of $\text{Fe}_{14}\text{Nd}_2\text{B}$ particles separated by a complex, and as yet not completely characterized Nd-rich region that forms around the matrix phase. It has been postulated [5] that these Nd-rich boundary regions consist of a glassy borate phase which provides solid-state nucleation sites for the precipitation of α -Fe and an fcc phase, tentatively identified as an oxide of Nd, as the result of post-sintering heat treatment.

Based upon prior positron annihilation results reported for crystalline metallic alloys, the magnitude of both τ_1 and I_1 obtained from the two component fit are consistent with this component being highly correlated with annihilation events occurring within the crystalline regions in this material. The observed changes in τ_1 and I_1 as a function of thermal exposure indicate a net decrease in the local electron density in these ordered regions and a small but statistically significant decrease in the fraction of annihilation events occurring in these regions, respectively. The increase in τ_1 could be due to a relaxation phenomenon, changes in the composition of the phases involved, or phase redistribution. Note that the major increase in τ_1 occurred as the result of the low temperature exposure, which did not appreciably reduce coercivity.

Bulk lifetimes for most metallic materials typically range between 100-300 psec. Thus, based on both the finite time resolution of the measurement system and the fact that this material is comprised of several crystalline metallic phases, it is most probable that the resolved short-lived component is influenced by annihilation events occurring in more than one crystalline phase. The observed changes associated with this component are therefore most likely a reflection of the integrated structural changes occurring in all the ordered phases that contribute to this component. Further resolution of this average component into lifetimes and intensities that can be associated with specific crystalline phases requires more specific information as to what phases are present and the magnitudes of their specific

annihilation rate constants (lifetimes). As discussed in the following section, a three component fit with a constraint placed on one component lifetime provides some encouraging results that are in agreement with the interpretation of the short lifetime component presented above.

The longer-lived component lifetime τ_2 and associated intensity I_2 are both noted to increase as a function of thermal exposure. There are two possible contributing sources theorized for this long-lived lifetime component. The sample treated at 1150C exhibited a gray surface scale that was not observed on any of the samples treated at low temperatures. Lifetime spectra were obtained for this sample set in both the as-heat treated condition and after the scale had been removed by grinding. Note that the changes recorded for τ_1 and I_1 as the result of scale removal are small in comparison to the corresponding changes noted for τ_2 and I_2 . This result indicates that the long-lived component is highly correlated with source-surface annihilation events. In addition, it is possible that the long-lived component is also associated with annihilation events occurring in the glassy regions surrounding the $\text{Fe}_{14}\text{Nd}_2\text{B}$ -rich matrix regions. The magnitude of the lifetime component τ_2 is in the range expected for ortho-positronium "pickoff" events, which is a specific annihilation mechanism which is known to occur in amorphous materials. Also, there is a systematic change in both τ_2 and I_2 as a function of thermally-induced changes in coercivity, which would not necessarily be expected if this component was associated entirely with source-surface annihilation events. Further experimental work is required to isolate the structural factors that contribute to this long-lived component.

Three Component Fit

As previously noted, without constraining any of the fitting parameters, statistically meaningful results could be obtained using only a two component fit. However, as noted earlier, the first component of the two component fit is probably representative of more than one annihilation environment. In an attempt to further resolve the lifetime spectra, a three component fit was employed with one of the component lifetimes constrained to 0.110 nsec, which corresponds to the bulk annihilation lifetime of $\alpha\text{-Fe}$ [6]. The decision to constrain one component lifetime to that associated with $\alpha\text{-Fe}$ was predicated on the fact that there is experimental evidence [5] that $\alpha\text{-Fe}$ precipitates via glass decomposition in the amorphous regions surrounding the $\text{Fe}_{14}\text{Nd}_2\text{B}$ -rich matrix as the result of thermal processing. The $\alpha\text{-Fe}$, consisting of ~10 nm precipitates, is highly dispersed, coarsens as a function of elevated temperature exposure, and is detectable only by TEM examination. The short component lifetime τ_1 extracted using the two component fit increases in magnitude as a function of thermal exposure. If a portion of this component is correlated with annihilation events occurring in the $\alpha\text{-Fe}$, then, as a function of coarsening, the iron contribution to this component would decrease, resulting in the observed increase in the component lifetime τ_1 .

Modeling the lifetime spectra with a partially constrained three component fit resulted in statistically valid and consistent results. The statistical uncertainty of the fit was found to be slightly higher than that obtained using the unconstrained two component fit, which at least in part can be attributed to the increased number of fitting parameters. Figure 2 shows

the thermally-induced variations in component lifetimes and their corresponding intensities as a function of coercivity. The corresponding standard deviations are given in Table II. The shortest component lifetime τ_1 was fixed at .110 nsec and the intermediate and longest component lifetimes τ_2 and τ_3 , as well as all three of the corresponding component intensities were fit using PFPOSFIT [2].

The results of the three component fit are consistent with the results previously discussed for the two component fit. The longest-lived component lifetime τ_3 and corresponding intensity I_3 are comparable to τ_2 and I_2 obtained using the two parameter fit, and are most likely composed of a source-surface contribution and perhaps a contribution from the glassy phase. As noted earlier, further experimentation is required to more completely characterize this component. Both the short-lived component τ_1 and I_1 and the intermediate component τ_2 and I_2 derived from the three component fit are related to the short-lived component τ_1 and I_1 extracted using the two component fit.

Note that I_1 extracted using the three component fit, which is associated with annihilation events occurring in α -Fe, decreases as a function of thermally-induced decreases in coercivity. This observation is consistent with the anticipated influence of particle coarsening on the positron annihilation component intensity, which has been documented to occur in Fe-Nd-B alloys as a function of elevated temperature exposure [5]. The intermediate component lifetime τ_2 and corresponding intensity I_2 were found to decrease and increase, respectively, as a function of thermally-induced decreases in coercivity.

With the contribution due to α -Fe effectively resolved, the intermediate component can be interpreted as reflecting changes in the annihilation environment associated with the remainder of the crystalline regions present in this Fe-Nd-B alloy. The observed reduction in τ_2 as a function of thermal exposure implies a general increase in the electron density, while the concomitant increase in I_2 is consistent with the smaller α -Fe contribution and an increasing degree of order within the material as a whole. Structurally, the reduction in τ_2 could be the result of a reduction in lattice parameter(s), a redistribution of the crystalline phases correlated with this annihilation component, or a reduction in the concentration of vacancy-type defects as the result of thermal exposure. The increase in the corresponding intensity component I_2 could be the result of recovery-recrystallization, grain growth, or some other thermally induced ordering mechanism. Further clarification of the thermally-induced structural changes associated with the observed variations in positron annihilation lifetime components requires further experimental work.

CONCLUSIONS AND FUTURE WORK

Although more questions have been raised than answered as the result of this short-term research project, the results are encouraging, and suggest that further positron annihilation studies combined with other characterization techniques may be useful in providing a more fundamental understanding of the relationship between structure and magnetic properties of R-Fe-B permanent magnetic materials. Specifically, the results of this study

demonstrate that the lifetime components extracted using either a two component or a partially constrained three component model are sensitive to thermally-induced structural changes and the concomitant reduction in coercivity in Fe-Nd-B alloys. Of particular significance is the demonstrated sensitivity of this technique in monitoring the presence and the redistribution of α -Fe as a function of thermal treatment.

Currently Dr. H. H. Stadelmaier and Dr. N. A. El-Masry are performing TEM studies on identically heat treated samples, which should aid in the further interpretation of our positron results. Additional complimentary characterization studies could include x-ray diffractometry, SEM/x-ray energy dispersive analysis and optical microscopy.

The results of this project suggest numerous additional short range and long range studies. Short range studies should be directed towards better characterization of:

1. the lifetime components associated with discrete phases known to be present in sintered Fe-Nd-B alloys
2. The surface-source component for this material
3. the relation between observed changes in coercivity and the corresponding changes in positron annihilation lifetime components.

Potentially useful long term studies involving the use of positron annihilation spectroscopy could include:

1. in-situ thermal studies, including thermal cycling
2. the effect of other rare-earth additions on structure and magnetic properties
3. the effects of hydrogenization on structure.

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Table I. Two Component Fit

Sample	Lifetimes (nsec.)			Intensities (%)	
		τ_1	τ_2	I_1	I_2
As-Received, Demagnetized	Mean	0.196	1.361	98.313	1.588
	Std. Dev.	0.001	0.016	0.075	0.075
Low Temperature Thermal Exposure	Mean	0.205	1.564	98.313	1.688
	Std. Dev.	0.001	0.077	0.060	0.060
High Temperature Thermal Exposure (with scale)	Mean	0.220	1.360	97.414	2.586
	Std. Dev.	0.001	0.049	0.077	0.077
High Temperature Thermal Exposure (scale removed)	Mean	0.206	1.639	97.985	2.015
	Std. Dev.	0.001	0.028	0.120	0.120

Table II. Three Component Fit

Sample	Lifetimes (nsec.)				Intensities (%)		
		τ_1	τ_2	τ_3	I_1	I_2	I_3
As-Received, Demagnetized	Mean	0.110	0.250	2.064	68.603	30.132	1.270
	Std. Dev.	---	0.011	0.107	6.421	6.421	0.037
Low Temperature Thermal Exposure	Mean	0.110	0.221	1.851	36.012	62.466	1.522
	Std. Dev.	---	0.002	0.069	2.503	2.535	.042
High Temperature Thermal Exposure	Mean	.110	0.217	1.880	26.485	71.692	1.822
	Std. Dev.	---	0.004	0.073	7.108	7.078	0.003

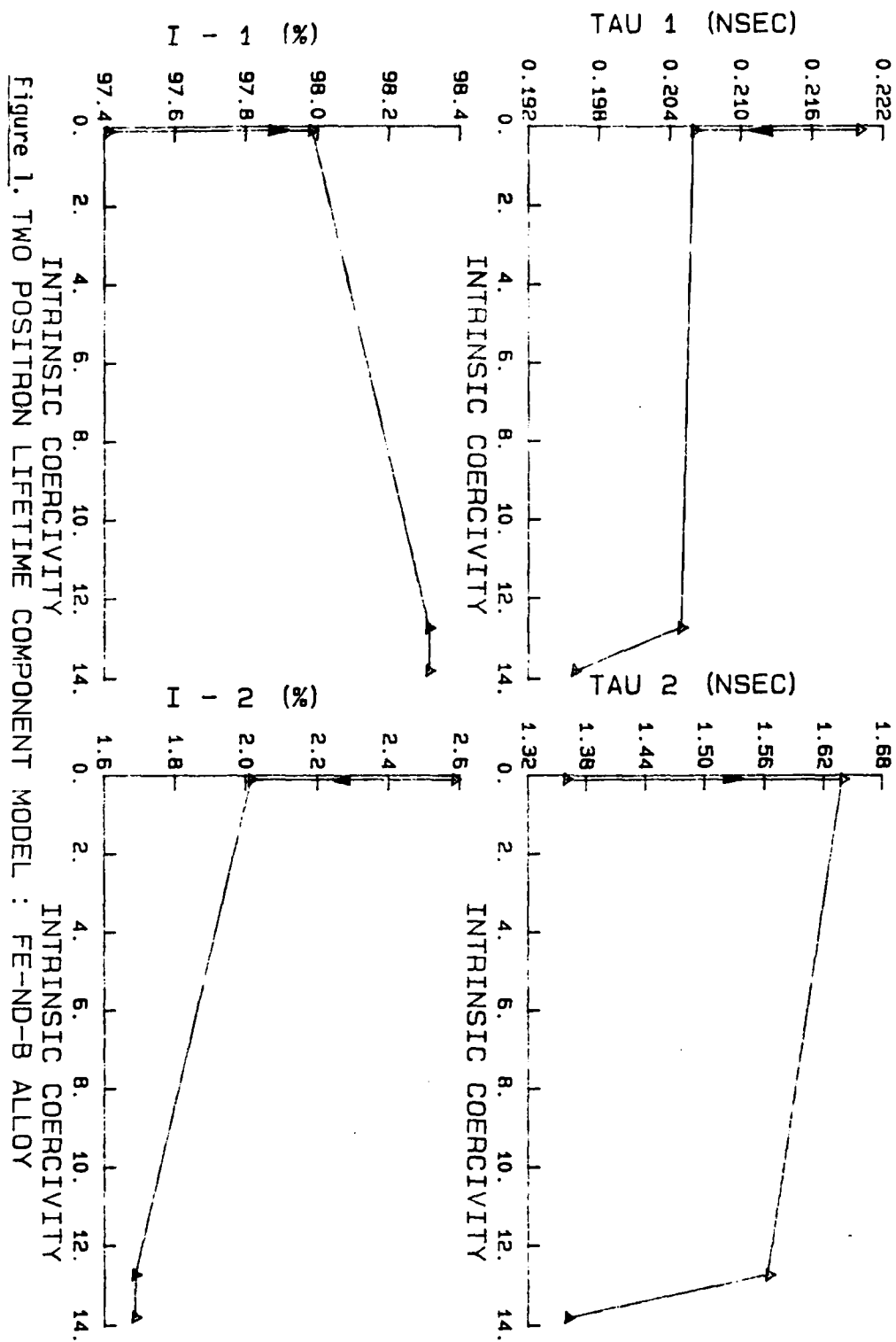


Figure 1. TWO POSITRON LIFETIME COMPONENT MODEL : FE-ND-8 ALLOY

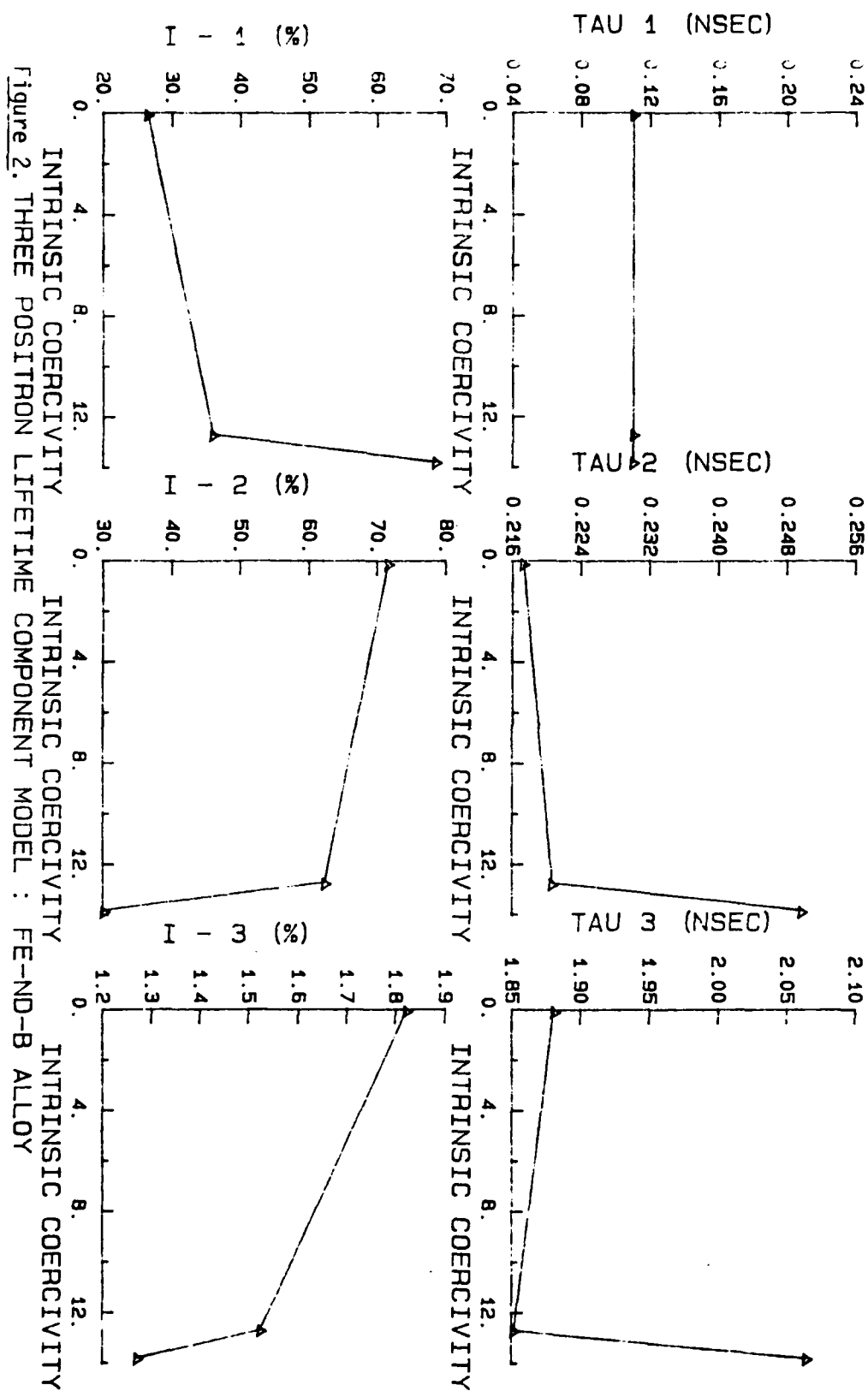


Figure 2. THREE POSITRON LIFETIME COMPONENT MODEL : FE-ND-B ALLOY

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